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Scope of Research

We perform kinetic and mechanistic analyses toward understanding chemical and physicochemical reactions occurring in polymerization systems and better routes for synthesis of well-defined polymers. In particular, new well-defined polymers or polymer assemblies are prepared by living polymerization techniques, and their structure-properties relationships are precisely analyzed. Projects in progress include: 1) kinetics and mechanisms of living radical polymerization (LRP); 2) synthesis of new polymeric materials by living polymerizations and their structure/properties studies; and 3) synthesis, properties, and applications of concentrated polymer brushes (CPB).



KEYWORDS

Precision Polymerization
Hybrid Materials

Living Radical Polymerization
Biointerface

Polymer Brush

Selected Publications

Tsujii, Y.; Nomura, Y.; Okayasu, K.; Gao, W.; Ohno, K.; Fukuda, T., AFM Studies on Microtribology of Concentrated Polymer Brushes in Solvents, *J. Phys.: Conf. Ser.*, **184**, 012031 (2009).

Arita, T.; Kayama, Y.; Ohno, K.; Tsujii, Y.; Fukuda, T., High-Pressure Atom Transfer Radical Polymerization of Methyl Methacrylate for Well-Defined Ultrahigh Molecular-Weight Polymers, *Polymer*, **49**, 2426-2429 (2008).

Tsujii, Y.; Ohno, K.; Yamamoto, S.; Goto, A.; Fukuda, T., Structure and Properties of High-Density Polymer Brushes Prepared by Surface-Initiated Living Radical Polymerization, *Adv. Polym. Sci.*, **197**, 1-45 (2006).

Ohno, K.; Morinaga, T.; Takeno, S.; Tsujii, Y.; Fukuda, T., Suspension of Silica Particles Grafted with Concentrated Polymer Brush: Effects of Graft Chain Length on Brush Layer Thickness and Colloidal Crystallization, *Macromolecules*, **40**, 9143-9150 (2007).

Ohno, K.; Morinaga, T.; Koh, K.; Tsujii, Y.; Fukuda, T., Synthesis of Monodisperse Silica Particles Coated with Well-Defined, High-Density Polymer Brushes by Surface-Initiated Atom Transfer Radical Polymerization, *Macromolecules*, **38**, 2137-2147 (2005).

Synthesis of Iron Oxide Rods Coated with Polymer Brushes and Control of Their Assembly in Thin Films

We investigated surface-initiated atom transfer radical polymerization (SI-ATRP) of methyl methacrylate (MMA) using monodisperse rod-type particles of iron oxide, β -FeOOH. The slow hydrolysis of iron(III) chloride yielded monodisperse β -FeOOH rods with an average length-to-width ratio, L/W , of 6 ($L = 210$ nm and $W = 35$ nm on average). The surface of the β -FeOOH rods was modified with a triethoxysilane derivative as an ATRP-initiating site, namely, (2-bromo-2-methyl)propionyloxypropyl triethoxysilane. The SI-ATRP of MMA, mediated by a copper complex, was performed using the initiator-coated β -FeOOH rods in the presence of a sacrificial free initiator. Well-defined poly(methyl methacrylate) (PMMA) brushes with molecular weights of up to 700,000 could be grafted on the β -FeOOH rods with a surface density as high as 0.3 chains/nm². The resultant polymer-brush afforded hybrid rods exhibited high dispersibility in various solvents for PMMA without forming aggregates. Thin films were prepared by dip-coating from a suspension of the hybrid rods and the rods were oriented in a specific direction in the films. The arrangement of the rods could be controlled by varying the chain length of the polymer brush and the withdrawal speed during the dip-coating process.

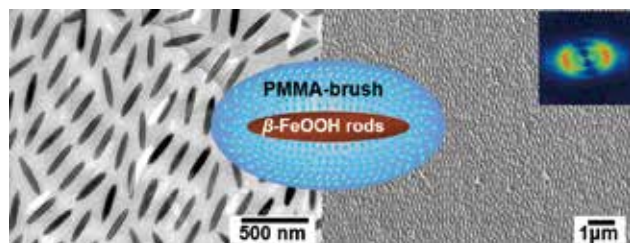


Figure 1. Transmission and scanning electron microscopy images of films of β -FeOOH rods end-grafted with PMMA.

Preparation of Polymer Monolith Materials by Using Block Copolymer Surfactants

The use of block copolymer-based surfactants has been proposed as a methodology for creation of various polymeric monolith materials, where monolith means bi-continuous skeletal and pore space with meso-/macroporous sizes. For example, freestanding epoxy-based monolith membranes have been developed through polymerization induced phase separation based on the spinodal decomposition with an assist of a PVA sacrifice film. The membranes are 10–20 μ m thick and a few centimeters on each side (Figure 2a), which could be applied for heat resistant separators of lithium ion secondary batteries. To improve their mechanical properties, cellulose nanofibers (CNFs) were introduced as a reinforcement filler, leading Young's modulus to be about 1.3 times higher than that of a neat monolith membrane. In addition, by using suitable block copolymers as a surfactant, the modulus increase was about twice higher than for a neat monolith, because the interfacial strength between monolith and CNFs was strong. Another example showed that block copolymer-stabilized emulsion could be used for the preparation of polymer monolith particles without a surface skin layer (Figure 2b). The composition of the block copolymer was crucial for the formation of skin on the surface, as well as the size of particles, interpreted by the interfacial tension parameter. These particles are promising for separation materials with application in chromatography, water purification, and adsorption of toxic substances.

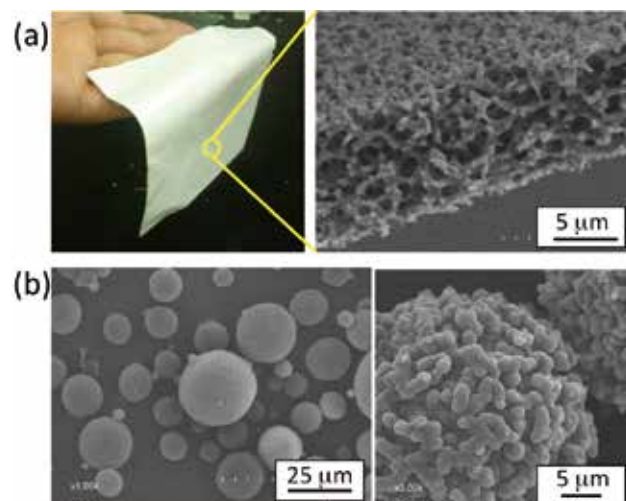


Figure 2. SEM images of polymer monolith materials in the form of (a) a sheet and (b) particles without a surface skin layer.